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Dedicated to blessed memory of our colleague Prof. A.A. Pasynskii

Specific Features of the Coordination of $[Ni(En)_2]^{2+}$ Cations to the $[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]^{8-}$ Cluster Anion

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Abstract—The cluster complex $(Me_4N)K_7[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 10H_2O$ (**I**) is synthesized by the high-temperature reaction of ReI_3 with KCN and subsequent recrystallization from an aqueous solution with the addition of Me_4NI. The anion of complex **I** contains ligands $\mu_3\text{-}CCN^{3-}$ stabilized due to coordination to the triangular faces of the $\{Re_4\}$ tetrahedral metal cluster. It is shown for $[Ni(En)_2]^{2+}$ as an example that the $\mu_3\text{-}CCN^{3-}$ ligands are ambidentate and can interact with transition metal cations similarly to the terminal CN groups, affording the coordination polymer $[Ni(En)_2(NH_3)_2][\{Ni(En)_2\}_3\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 7.5H_2O$ (**II**). The structures of complexes **I** and **II** are determined by X-ray diffraction analysis (CIF file CCDC nos. 2057450 (**I**) and 2057451 (**II**)).

Keywords: rhenium, tetrahedral cluster complexes, crystal structure, coordination polymer

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INTRODUCTION

Cluster compounds of group 5–7 transition metals have been studied for several decades due to their structural diversity and manifested physicochemical properties. Bright luminescence in the red and near-IR ranges [1–3] and reversible redox transformations [4, 5] can be distinguished among the most interesting properties of these compounds. The use of the molybdenum, tungsten, and rhenium cluster complexes as building blocks for the synthesis of functional coordination polymers is an interesting and poorly studied area [6–8]. The high symmetry and large volume of the cluster complexes make them convenient for the design of crystalline coordination polymers and metal-organic frameworks, whereas the spectroscopic and redox characteristics of the clusters can be used to impart desirable properties to the obtained product [5]. The properties of the cluster compounds are determined by both the composition and geometry of the cluster core and, hence, the search for the synthesis methods of new cluster complexes remains an urgent task.

For several recent years we studied the formation of cluster phases by the reactions of molybdenum, tungsten, and rhenium oxides and iodides with inorganic cyanides at the temperatures from 350 to 550°C [9–15]. The occurrence of these reactions at the temperatures lower than the melting points of the corresponding cyanides is their characteristic feature. We showed that the use of oxides and iodides as the starting compounds at relatively low synthesis temperatures provided the possibility of preparing compounds with cluster cores of new types and/or unusual internal ligands. The bitetrahedral tungsten complexes with the $\mu_3\text{-}CCN^{3-}$ ligands [15] or the tetrahedral rhenium complexes with the $\mu_3\text{-}PO^{3-}$, $\mu_3\text{-}PO_2^{3-}$, $\mu_3\text{-}As^{3-}$, and $\mu_3\text{-}AsO^{3-}$ ligands [9, 16] can be presented as examples.

In this work, we continue our studies on the synthesis of rhenium cluster complexes from ReI_3 and report the synthesis and structure of the new tetrahedral cluster $(Me_4N)K_7[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 10H_2O$ (**I**). This complex was synthesized by the reaction of ReI_3 with KCN excess at 480°C followed by recrystallization from water with the addition of Me_4NI. The further reaction of compound **I** with $[Ni(En)_2]Cl_2$ (En is ethylenediamine) in concentrated ammonia afforded the coordination polymer $[Ni(En)_2(NH_3)_2][\{Ni(En)_2\}_3\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 7.5H_2O$ (**II**). In this compound, the CCN^{3-} ligands are ambidentate and participate in the formation of the polymeric framework.

EXPERIMENTAL

Rhenium iodide ReI_3 was synthesized using a known procedure [17]. Other reagents and solvents were used as commercially available reagents without additional purification. The ratio of heavy elements was determined by energy dispersive elemental analysis (EDS) on a Hitachi TM3000 TableTop SEM desktop scanning microscope using the Bruker QUANTAX 70 EDS equipment. Elemental analysis was carried out on a Euro-Vector EA3000 Elemental Analyzer instrument. IR spectra in a range of 4000–400 cm^{-1} were recorded for the samples prepared as pellets with potassium bromide on a Bruker Vertex 80 spectrometer.

Synthesis of $(Me_4N)K_7[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 10H_2O$ (I). A mixture of ReI_3 (0.300 g, 0.53 mmol) and potassium cyanide (0.345 g, 5.30 mmol) was thoroughly triturated in a mortar and placed in a quartz ampule, which was evacuated and sealed. The ampule was heated to 480°C for 4 h, kept at this temperature for 72 h, and cooled with a rate of 50°C/h. *Attention! Highly toxic dicyan can evolve after opening of the ampule.* The reaction products were dissolved in water, refluxed, and filtered off. The solution was added by Me_4NI (0.200 g), and the mixture was evaporated to 3 mL and cooled to room temperature. The target product as red crystals suitable for X-ray diffraction analysis (XRD) was isolated by the diffusion of MeOH vapors to the obtained aqueous solution. The yield of compound **I** was 0.078 g (34%).

EDS: K : Re = 6.8 : 4.0. IR (ν, cm^{-1}): 1616 δ(OH), 2130, 2086, 2065 ν(CN), 3432 ν(OH).

For $C_{24}H_{32}N_{17}O_{10}K_7Re_4$

Anal. calcd., %	C, 16.59	H, 1.85	N, 13.71
Found, %	C, 16.51	H, 1.64	N, 13.79

Synthesis of $[Ni(En)_2(NH_3)_2][\{Ni(En)_2\}_3\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 7.5H_2O$ (II). A solution of $[Ni(En)_2]Cl_2$ (0.015 g, 0.06 mmol) in a 30% aqueous solution of ammonia (5 mL) was carefully layered onto a solution of $(Me_4N)K_7[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 10H_2O$ (0.020 g, 0.012 mmol) in H_2O (5 mL) in a glass tube. The dark red crystals formed in a week were filtered off and dried on a paper filter. The yield of compound **II** was 0.022 g (87%).

EDS: Ni : Re = 4.1 : 4.0. IR (ν, cm^{-1}): 1618 δ(OH), 2132, 2098, 2074 ν(CN), 2800–3000 ν(CH), 3312, 3261 ν(NH), 3454 ν(OH).

XRD of compounds **I** and **II** was carried out on a Bruker-Nonius X8 Apex automated diffractometer using MoK_α radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. An absorption correction was applied by intensities of equivalent reflections (SADABS) [18]. The structure was solved by a direct method and refined by full-matrix least squares for F^2 in the anisotropic approximation for non-hydrogen atoms (SHELXL) [19]. The hydrogen atoms of the NH_3 and En ligands in compound **II** were localized geometrically. The hydrogen atoms of the solvate water molecules were not localized. The figures were drawn using the DIAMOND program [20]. Selected crystallographic data and structure refinement parameters for compounds **I** and **II** are presented in Table 1.

The atomic coordinates and other parameters of the structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2057450 (**I**) and 2057451 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

It has recently been shown that ReI_3 is a promising precursor for the synthesis of new rhenium clusters at the temperatures at which other starting compounds remain inert. For example, the reaction of ReI_3 with KCN at 480°C affords complex $K_8[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 5H_2O\cdot KCN$ [9]. The compound is stable in air and demonstrates an excellent solubility in H_2O. However, attempts to dissolve the synthesized complex in other available solvents were unsuccessful.

We hoped to go from aqueous to organic solutions and, hence, attempted to obtain the salt with the organic cation by the addition of Me_4NI to the system. After the single crystals were obtained and their crystal structure was determined by the XRD method, we found that the complex $(Me_4N)K_7[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 10H_2O$ (**I**) was the product in the case of using Me_4NI (which was confirmed by the elemental analysis data). Being a potassium salt, compound **I** turned out to be soluble in water only.

According to the structural data, compound **I** crystallizes in the cubic crystal system with the space group *F*-43*m*, *Z* = 4. The crystal structure of compound **I** contains the cluster anion $[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]^{8-}$ (Fig. 1), seven K^+ cations, one Me_4N^+ cation, and ten uncoordinated water molecules. The structure of the anion in compound **I** is most close to the structures of the chalcocyanide complexes $[\{Re_4Q_4\}(CN)_{12}]^{n-}$ (Q = S^{2-}, Se^{2-}, Te^{2-}) [21–23] and recently synthesized pnictogen-containing complexes of the $[\{Re_4X_4\}(CN)_{12}]^{n-}$ type (X = PO^{3-}, PO_2^{3-}, As^{3-}, AsO^{3-}) [9, 10, 16]. This is a typical 12-electron cluster complex containing six two-electron metal–metal bonds, but the Re–Re bond length (2.6837(14) Å) is noticeably shortened (~0.05–0.20 Å) compared to the values observed in the aforementioned compounds. The μ_3-bridging CCN^{3-} ligand coordinates via the trigonal-pyramidal mode to each face of the Re_4 tetrahedron with the $Re–C_{CCN}$ distance equal to 2.07(2) Å. The geometric parameters of the μ_3-CCN^{3-} ligands are

Table 1. Crystallographic data and structure refinement parameters for compounds **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{24}H_{32}N_{17}O_{10}K_7Re_4$	$C_{36}H_{86}N_{34}O_{7.5}Ni_4Re_4$
FW	1737.16	2103.02
Crystal system	Cubic	Monoclinic
Space group	*F*-43*m*	*P*2$_1$/*c*
a, Å	16.9835(9)	14.7439(3)
b, Å	16.9835(9)	20.5652(4)
c, Å	16.9835(9)	22.7708(5)
α, deg	90	90
β, deg	90	90.3290(10)
γ, deg	90	90
V, Å^3	4898.7(8)	6904.2(2)
Z	4	4
ρ_{calc}, g/cm^3	2.355	2.023
μ, mm^{-1}	10.509	8.112
F(000)	3232	3720
Crystal sizes, mm	0.08 × 0.08 × 0.08	0.28 × 0.26 × 0.10
Ranges of indices *h*, *k*, *l*	$-19 \le h \le 19$, $-22 \le k \le 22$, $-22 \le l \le 22$	$-15 \le h \le 19$, $-26 \le k \le 18$, $-29 \le l \le 29$
Measured reflections	6080	44 052
Independent reflections	615	15796
R_{int}	0.0521	0.0262
Reflections with $I > 2\sigma(I)$	586	14224
R_1, wR_2 ($I > 2\sigma(I)$)	0.0316, 0.0816	0.0329, 0.0795
R_1, wR_2 (all reflections)	0.0337, 0.0827	0.0390, 0.0815
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	−0.743/1.019	−1.264/2.815

well consistent with those reported previously [13, 15, 24, 25]: the C–C and C–N bond lengths are 1.47(5) and 1.13(4) Å, respectively.

One of the interesting properties of the $[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]^{8-}$ anion is the ambidentate character of the CCN^{3-} ligands and their participation in the formation of the framework of the coordination polymer $[Cu(En)_2][Cu(En)(NH_3)_2]_3[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot5H_2O$ [13]. In this work, we continued to study the possibility of using the $[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]^{8-}$ anion as a building block. For example, the reaction of compound **I** with $[Ni(En)_2]Cl_2$ in concentrated ammonia afforded the $[Ni(En)_2(NH_3)_2][\{Ni(En)_2\}_3\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot7.5H_2O$ polymer (**II**).

Compound **II** crystallizes in the monoclinic crystal system with the space group *P*2$_1$/*c*, *Z* = 4. The geometric parameters of the cluster anion are similar to those in compound **I**. In particular, the Re–Re and Re–C_{CCN} bond lengths vary in the ranges 2.6713(3)–2.6961(3) and 2.071(5)–2.104(5) Å, and the C–C and C–N bond lengths in the CCN^{3-} ligands are 1.402(8)–1.417(8) and 1.162(9)–1.174(9) Å, respectively.

The cationic moiety of compound **II** contains four symmetrically independent nickel(II) ions, one of which has a distorted octahedral structure and coordinates two NH_3 ligands and two En ligands. Three other nickel(II) ions coordinate two En ligands only, resulting in the formation of the planar square $[Ni(En)_2]^{2+}$ complexes. These species participate in bridging interactions with five cyanide ligands of each $[Re_4(CCN)_4(CN)_{12}]^{8-}$ anion (Fig. 2). Three of five bridging CN^- ligands belong to one rhenium atom, and two ligands belong to another atom, whereas the

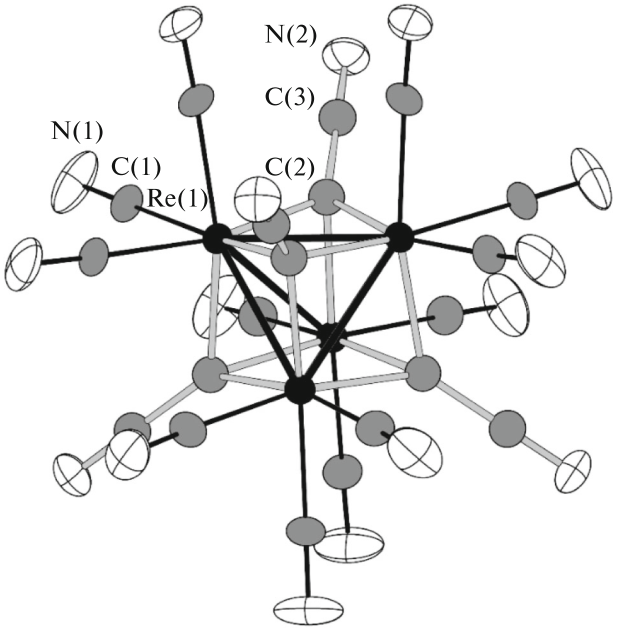

Fig. 1. Structure of the $[Re_4(CCN)_4(CN)_{12}]^{8-}$ cluster anion. Thermal ellipsoids of 30% probability are presented.

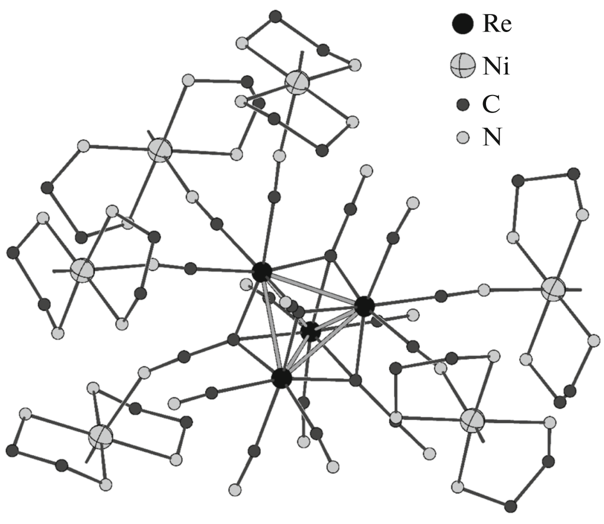

Fig. 2. Bridging interactions of the $[Ni(En)_2]^{2+}$ cations with the CN^- and CCN^{3-} ligands of the $[Re_4(CCN)_4(CN)_{12}]^{8-}$ anion in the structure of compound **II**.

CN^- ligands of the remained rhenium atoms are not involved in coordination with the $[Ni(En)_2]^{2+}$ cation. The lengths of the bridging $Ni-N_{CN}$ bonds (2.068(5)–2.098(5) Å) are comparable with the $Ni-N_{NH3/En}$ bond lengths (2.075(7)–2.112(6) Å). In addition, one of the CCN^{3-} ligands of each $[Re_4(CCN)_4(CN)_{12}]^{8-}$ anion forms the Re–CCN–Ni contact ($Ni-N_{CCN}$ 2.170(6) Å), which makes all Ni(II) centers hexacoordinated. Numerous bridging cyanide interactions in

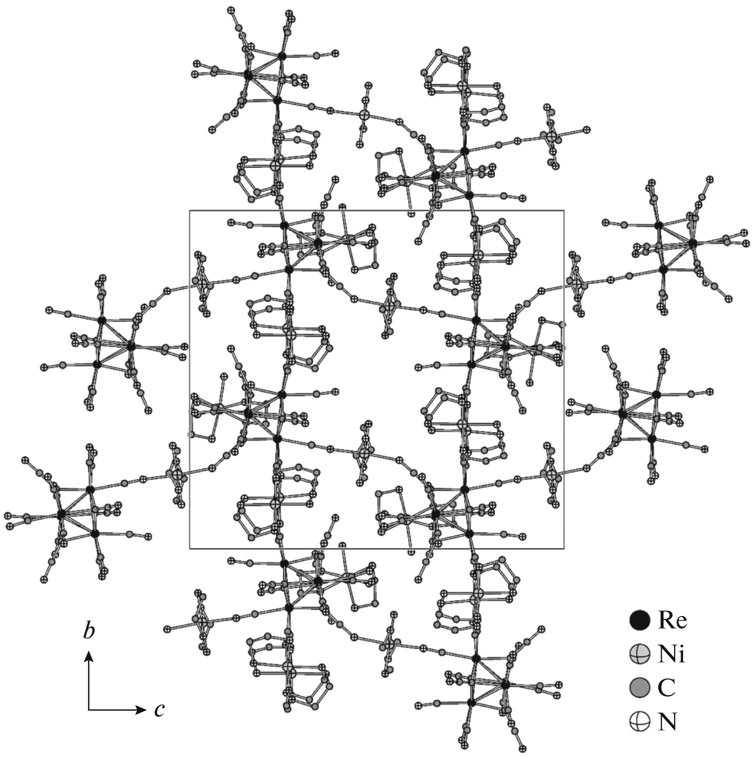

Fig. 3. Packing of the $[Ni(En)_2]^{2+}$ cations and $[Re_4(CCN)_4(CN)_{12}]^{8-}$ anions along the crystallographic axis *a* in the structure of compound **II**.

compound **II** and hydrogen bonds involving the NH_3, En, CCN^{3-}, and CN^- ligands and solvate H_2O molecules result in the formation of the three-dimensional framework as shown in Fig. 3.

Thus, the tetrahedral rhenium cluster complex $(Me_4N)K_7[\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 10H_2O$ was synthesized by the reaction of ReI_3 with KCN excess at 480°C followed by crystallization from water with the addition of Me_4NI. The further reaction of the synthesized compound with $[Ni(En)_2]Cl_2$ in concentrated ammonia afforded the coordination polymer $[Ni(En)_2(NH_3)_2][\{Ni(En)_2\}_3\{Re_4(\mu_3\text{-}CCN)_4\}(CN)_{12}]\cdot 7.5H_2O$ in which the CCN^{3-} ligands manifested the ambidentate character and participated in the formation of the polymer framework. The crystal structures of the synthesized compounds were determined by the XRD method.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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